

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
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1. AGENCY USE ONLY (Leave Blank)		2. REPORT DATE 30 June 1998		3. REPORT TYPE AND DATES COVERED Progress Report: 1 April 98 - 30 June 98
4. TITLE AND SUBTITLE Processing of Nanocrystalline Nitrides and Oxide Composites			5. FUNDING NUMBERS G - N00014-95-1-0626	
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9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 North Quincy Street Ballston Tower One Arlington, VA 22217-5660			10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The direct synthesis of nanocrystalline AlN in the forced flow reactor is described, along with initial characterization and chemical analysis results. The AlN has a surface area in excess of 100 square meters per gram and a volume average crystallite size of 40 nm. The particles are not entirely spherical and show some faceting and elongation, which explains the discrepancy between the high surface area and the XRD determined crystallite size.				
14. SUBJECT TERMS Nanocrystalline, Nitridation, Aluminum, Aluminum Nitride, Ammonia			15. NUMBER OF PAGES 3	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED		18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED		19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED
				20. LIMITATION OF ABSTRACT UL

19980714 072

"Processing of Nanocrystalline Nitrides and Oxide Composites"

Technical Report on ONR Grant No. N00014-95-1-0626
for the period of April 1, 1998 - June 30, 1998

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Nitridation of Nanocrystalline Aluminum

As reported previously[1], the synthesis of nanocrystalline aluminum can be easily accomplished in the forced flow reactor. The material produced is ultrafine-grained (30-50 nm, depending on the synthesis conditions) and appears to be equiaxed from X-ray diffraction (XRD) and electron microscopy. The material is readily nitrided to 70% conversion by 660°C (the melting point of aluminum) and can be further nitrided to >90% pure AlN by continued heating to 1000°C under a nitrogen flow. Kinetic analysis and determination of the activation energy for the low-temperature nitridation have been difficult, possibly due to surface oxidation or particle agglomeration affecting the mass transport of nitrogen to the particles. Additional experiments are currently underway to determine which factors affect the nitridation, and may include changing the reactant gas from nitrogen to ammonia.

Nanocrystalline Aluminum Nitride Synthesis

Our recent investigations into producing nanocrystalline aluminum nitride directly in the reactor have been met with considerable success[2]. Previously, we were able to synthesize only small amounts of pure AlN if we sublimed AlN powder into a nitrogen stream with the microwave plasma applied. This procedure required very high temperatures (~2000°C) to sublime the AlN and, partially due to the microwave plasma, produced only a small amount of powder. Larger quantities of a lower purity AlN powder (with excess aluminum) could also be produced if we evaporated aluminum metal under similar conditions. The excess aluminum was most likely due to periods of rapid evaporation and spattering just after an evaporation pellet has been added, producing significant amount of molten aluminum. By redesigning the feed stream and changing the operating conditions, a more even evaporation of material has been achieved. The feed material was changed from pellets to high-purity aluminum wire, and the nitriding gas was changed from nitrogen to ammonia. By heating the graphite crucible to approximately 1500°C before adding the aluminum, flash evaporation conditions can be attained. The aluminum wire also allows the addition of smaller amounts of aluminum each time, producing a more uniform evaporation and preventing the accumulation of molten aluminum. In the current configuration, the ammonia is added upstream of the crucible and can nitride the molten aluminum in the crucible unless high temperatures are used to rapidly and completely evaporate

the aluminum wire as it is introduced. Since the ammonia begins to decompose spontaneously at temperatures greater than 200°C [3] and is then free to react with the aluminum, the microwave plasma is not needed. X-ray diffraction patterns of the white as-synthesized powder and the heat treated sample are shown in Figure 1. The as-synthesized powder has a crystallite size of approximately 40 nm, which increases to approximately 45 nm after heat

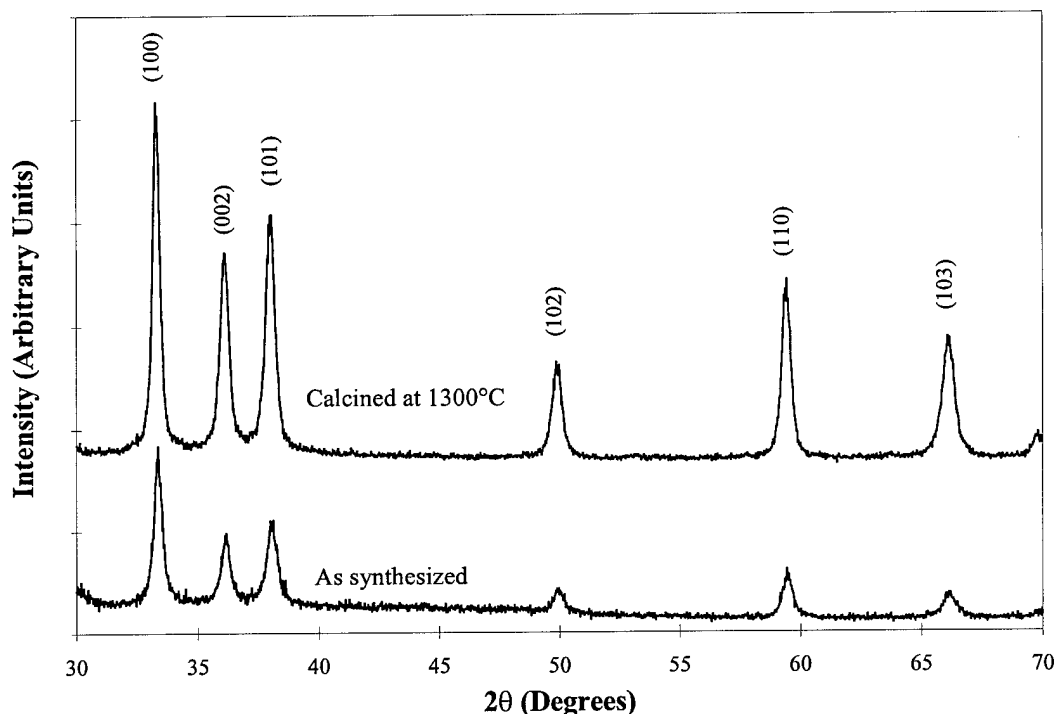


Figure 1. X-ray diffraction pattern of AlN powder as synthesized and after calcining at 1300°C in nitrogen for three hours.

treatment at 1300°C. The surface area of the powder as synthesized is 119 m²/g, which corresponds to an equivalent spherical diameter of 16 nm. However, the particles are not entirely spherical, as observed by transmission electron microscopy, but range from brick-shaped particles with an aspect ratio of approximately 2 or 3 to nearly spherical particles. In these preliminary runs, the reactor pressure increased from 3 mbar to 25 mbar as the run proceeded, so it is difficult to determine under what conditions the various particle morphologies were produced. The effect of various synthesis parameters, such as reactor pressure, ammonia concentration, ammonia inlet location and gas velocity, on particle size, morphology, and purity will be examined in future experiments.

Unlike the particles produced from subsequent nitridation of nanocrystalline aluminum which displayed an obvious XRD orientation preference for the (002) direction[1], the relative intensities of the XRD peaks for directly nitrided nanocrystalline AlN (Figure 1) are nearly identical to those of uniform polycrystalline AlN. In addition, the in-situ synthesized aluminum nitride does not display any oxygen-containing phases (such as γ - or α -Al₂O₃ or any of the aluminum oxynitride phases) after calcination, whereas the post-synthesis nitrided nanocrystalline aluminum exhibited these secondary phases.

These preliminary runs resulted in a material that was approximately 31.55 wt% N, and 57.3 wt% Al. (The stoichiometry of pure AlN is 34.2 wt% N and 65.8 wt% Al.) The missing mass is made up of carbon (~1 wt%), hydrogen (~0.65 wt%), and, most probably, oxygen (by difference, ~9.5 wt%). The source of the carbon may be adsorbed hydrocarbon on the high surface area AlN or contamination from the graphite crucible. The chemistry of the carbon in the sample is unknown since both graphite and aluminum carbide (Al_4C_3) are present in the crucible at these high temperatures and both could be transported in the gas stream along with the AlN. The source of the oxygen is undetermined; however, since the powder is exposed to the air for a short period of time before chemical analysis, it could pick up surface oxygen, water, or hydrocarbons during this time. The stoichiometry of these powders is apparently nitrogen-rich and roughly corresponds to a formula of $\text{AlN}_{1.06}(\text{OH})_{0.28}\text{C}_{0.04}$. Direct analysis of oxygen content in unexposed samples using fast neutron activation analysis is being planned. Future work on improving the chemical purity of the AlN will involve changing the reactor conditions and raw materials (aluminum supply, gas purity, etc.), as well as improving powder handling methods if deemed necessary.

[1] Ying, J.Y. "Technical Report on ONR Grant No. N00014-95-1-0626 for the period of January 1, 1998 - March 31, 1998"

[2] Panchula, M.L. and Ying, J.Y., M.I.T., unpublished results.

[3] Huseby, I. C. "Synthesis and Characterization of a High-Purity AlN Powder" *J. Am. Ceram. Soc.* **66** [3] 217-220, (1983).